



Short communication

Positron annihilation lifetime study of Nafion/titanium dioxide nano-composite membranes



M. Lei^{a,b}, Y.J. Wang^b, C. Liang^b, K. Huang^b, C.X. Ye^b, W.J. Wang^{c,*}, S.F. Jin^c, R. Zhang^{a,b}, D.Y. Fan^b, H.J. Yang^b, Y.G. Wang^b

^aState Key Laboratory of Information Photonics and Optical Communications, Beijing University of Posts and Telecommunications, Beijing 100876, China

^bSchool of Science, Beijing University of Posts and Telecommunications, Beijing 100876, China

^cBeijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

HIGHLIGHTS

- PAL is applied to investigate size and number density of free volumes in Nafion/TiO₂ membrane.
- The proton transporting ability is correlated with the properties of free volume.
- PAL is powerful for illuminating the relationship between structure and ion transport.

ARTICLE INFO

Article history:

Received 27 May 2013

Received in revised form

4 August 2013

Accepted 5 August 2013

Available online 15 August 2013

Keywords:

Polymer electrolyte membrane

Titanium dioxide nanoparticles

Humidity

Positron

Free volume

ABSTRACT

Positron annihilation lifetime (PAL) technique is applied for investigation of size and number density of free volumes in Nafion/TiO₂-nanoparticles composite membrane. The proton transporting ability is correlated with the properties of free volume inside the membrane. It is revealed that composite membrane with 5 wt% of TiO₂ nano-fillers exhibits good electrochemical performance under reduced humidity and it can be saturated with water at relative humidity of 50%, under which ionic clusters and proton transporting channels are formed, indicating that composite membranes with 5 wt% of TiO₂ nano-fillers are effective electrolyte for fuel cells operated at reduced humidification levels. The results suggest that PAL can be a powerful tool for elucidating the relationship between microstructure and ion transport in polymer electrolyte membranes.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

In the past decades, considerable attention has been paid on the development of polymer electrolyte membrane fuel cell (PEMFC) as portable, transportation, and stationary energy sources because of its high power density and zero-emission [1]. As restricted by proton conduction mechanism, high humidification condition is generally required for the state of the art of PEMFC to ensure the effective proton transportation inside the polymer electrolyte membrane (PEM) that is one of the key materials in PEMFC [2]. The thus-applied humidification sub-system can not only decrease the power density, but also increase the cost of the system. Thus, PEMFC operated under reduced humidification levels is of great importance for its further widespread applications.

One technical challenge for PEMFC operated under less-humidified condition is the membrane electrolyte that should maintain reasonable proton conductivity under reduced humidification level of fuel gases. The often used electrolyte materials for PEMFC are perfluorosulfonated ionomers, known as Nafion from DuPont. However, the strong humidity-dependent proton conductivity of Nafion membranes limited their applications under relatively low humidification conditions [2]. Although alternative electrolyte membranes have been developed for less-humidified PEMFC applications as described in recent reviews [3–5], perfluorosulfonated ionomer membranes are still the most important electrolyte materials for PEMFC because of their robust structure and excellent physicochemical properties [2]. Thus, modification of perfluorosulfonated membranes remains an active research area for less-humidified PEMFCs.

One interesting approach for modification of perfluorosulfonated membranes is to impregnate hygroscopic metal oxide nanoparticles into the membranes to enhance the water retention ability of

* Corresponding author. Tel./fax: +86 10 82649032.

E-mail address: wjwang@iphy.ac.cn (W.J. Wang).

membranes through surface hydroxyl groups and accordingly to improve the proton conductivity of membranes under less humidified conditions [6–9]. Although the amount of retained water in such nanocomposite membranes increases with the increase in concentration of doped metal oxides, the proton conductivity exhibits a non-monotonic behavior with the impregnated concentration of metal oxide fillers [7]. It has been proposed that the impregnated less proton-conductive materials may block the proton transporting pathway at relatively high concentration of metal oxide fillers [10]. However, no experimental evidence to confirm this hypothesis has been reported. This has led our interest to positron annihilation lifetime (PAL) study to elucidate how the microstructure affects the proton transportation inside the nanocomposite membranes since PAL technique has been successfully applied for sensitively probing the microstructure and transfer properties of small molecules in various polymeric membranes [11,12].

For the general PAL technique, positrons are emitted from a radioactive positron source associated with gamma-rays as starting signal. While positrons are injected to solid materials, they will annihilate through interaction with electrons, releasing new detectable gamma-rays. The lifetime of positron can be therefore determined according to the time between the starting signal and the generated signals. If voids are present in the materials, positrons will reside in them and the annihilation process can be delayed. Thus, the lifetime of positrons can be applied to determine the microstructure of materials. The PAL spectroscopy generally provides three types of lifetime corresponded to three intensities in polymeric membranes using PATFIT fitting program. The shortest lifetime τ_1 and the medium lifetime τ_2 correspond to *para*-positronium self-annihilation and free positron annihilation, respectively, whereas the longest lifetime τ_3 relates to *ortho*-positronium (*o*-Ps) pickoff annihilation. The *o*-Ps pickoff annihilation lifetime τ_3 and corresponding intensity I_3 are closely related to the free volume element size and number density that can be determined based on Tao–Eldrup model. Free volume has been correlated to macroscopic properties such as viscoelastic, rheological, and transporting properties of polymeric materials [13,14]. Particularly, free volume has been applied to polymer electrolyte membranes to explain the gas crossover behavior under different environment. For example, Mohamed et al. [11] have investigated oxygen and hydrogen permeabilities of Nafion membrane, commercialized perfluorosulfonated membrane from DuPont, under different humidification levels using PAL technique and pointed out that gas permeation in the membrane at dry state is governed by the free volume. In this paper, we discuss the correlation of proton transportation with the concentration of hygroscopic metal oxide fillers and relative humidity in a model polymer electrolyte nanocomposite membrane consisting of Nafion ionomers and TiO₂ nanoparticles.

2. Experimental

2.1. Formation of nano-composite membranes

In this work, commercial Nafion® dispersion (DuPont, Ew 1100, 5 wt% in isopropanol/water of about 95:5) were evaporated 120 °C and re-dissolved in *N*-methyl-2-pyrrolidone. The desired quantity of tetrabutyl titanate solutions was added dropwise to the Nafion® solution under vigorous stirring in an inert nitrogen atmosphere at 120 °C and allowed to cool down to 40 °C. After adjusting the pH of the dispersion to ~2.0 using 2 M HCl solution, the mixture was continuously stirred for 8 h at 40 °C to ensure the complete hydrolysis of precursor molecules. The formed dispersion containing Nafion and hydrolyzed titanate nanoparticles was then placed in a Petri dish, followed by the solvent evaporation at 100 °C for 8 h and post-treated at 150 °C under vacuum for 3 h. The formed membranes were then cleaned using a standard procedure at 80 °C for

30 min in 5% H₂O₂ solution, in de-ionized water, in 0.5 M H₂SO₄ solution, and finally in de-ionized water again. Fig. 1 displayed the schematic process of the formation of nanocomposite membranes.

2.2. Zeta potential measurements

Zeta potential measurements were carried out on Zetasizer Nano-ZS (Malvern, UK) using laser Doppler velocimetry and phase analysis light scattering. The temperature of the scattering cell was 25 °C and the data were analyzed with the software from supplier. Dynamic light scattering measurements were carried out with Malvern HPPS Laser Particle Size Analyzer (Malvern, UK) with scattering angle of 90° at 25 °C using He–Ne laser (633 nm). Concentration of dispersion for light scattering measurements is about 0.1 mg ml⁻¹. The size of formed nanoparticles was examined using high resolution transmission electron microscopy (TEM, JEM-2010FEF equipped with Energy Dispersive Spectrum Analyzer). Samples for TEM measurements were prepared by directly placing a drop of the solution on a thin carbon film supported by a copper grid.

2.3. Water uptake test

The water-uptake of membranes was calculated as the ratio of the difference between the swollen and the dry weight of the membrane. The weight of swollen membrane was measured rapidly after keeping the membrane at the set temperature under desired relative humidity for more than 4 h in a homemade chamber. The weight of the completely hydrated membrane was measured after boiling the membrane in de-ionized water for 24 h and wiping out the surface adsorbed water.

2.4. Proton conductivity measurement

The proton conductivity measurements were performed on an impedance analyzer (AutolabFG30/FRA, Eco Chemie) in the

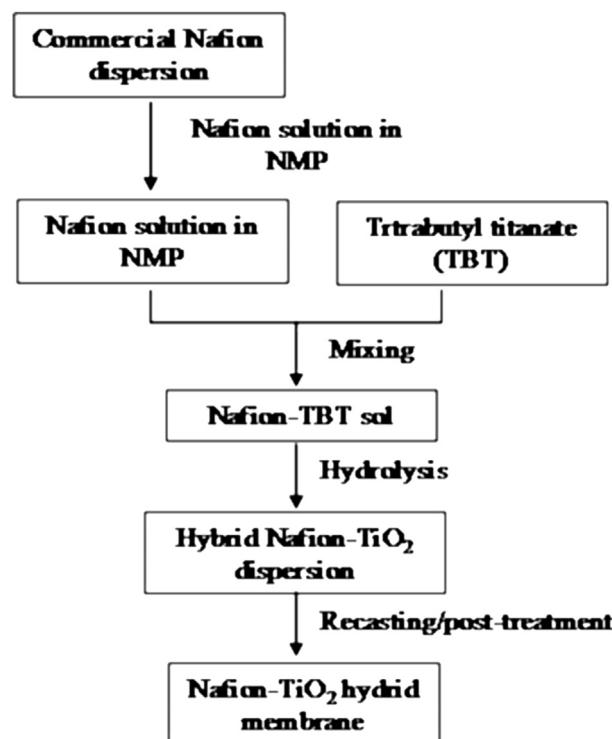


Fig. 1. Synthetic process of Nafion/TiO₂ nanocomposite membranes.

frequency range of 10 Hz and 100 KHz and the signal amplitude of 10 mV using a homemade testing chamber with controlled temperature and relative humidity. The resistance of the tested membrane was estimated from Cole–Cole plots and the proton conductivity was calculated using the thickness of the membrane and the electrode area.

2.5. Positron annihilation lifetime and intensity measurement

The ^{22}Na source (1 MBq in Kapton) was sandwiched by 10–20 pieces of membranes. The sandwiched sample in sample bag made from Al foil was then placed between two probes in a special testing chamber with controllable relative humidity and temperature. The relative humidity was controlled by humidifying nitrogen gases and detected with a sensor. Lifetime spectra were recorded on positron annihilation spectrometer with resolution of 276 ps and 1 million counts were collected for each measurement. The spectra were deconvoluted using PATFIT program and τ_1 , τ_2 , and τ_3 with corresponding I_1 , I_2 , and I_3 could be obtained.

3. Results and discussion

The Nafion– TiO_2 nanocomposite membranes were fabricated using a solvent casting process as reported in literature [15]. The TiO_2 nanoparticles were formed by in situ hydrolysis of desired amount of tetrabutyl titanate precursor in Nafion dispersion under acidic condition ($\text{pH} \sim 2.0$). At pH value of 2.0, TiO_2 nanoparticles are positively charged as indicated by zeta potential value of about 27 mV, whereas the negatively charged Nafion has the zeta potential of about –20 mV. Thus, Nafion molecules are expected to be adsorbed onto the surface of in situ formed TiO_2 nanoparticles through electrostatic interaction. This was confirmed by the increased zeta potential to about –53 mV of Nafion– TiO_2 nanoparticles dispersion, resulted from the concentrated sulfonic acid groups on the surface of TiO_2 nanoparticles. The electrostatic interaction between sulfonic acid groups on Nafion and the in situ formed TiO_2 nanoparticles makes the metal oxide fillers well distributed in the following formed membranes with typical thickness of 80 μm .

One of the very important properties that a qualified fuel cell membrane should have is the proton conductivity that determines the performance of the assembled fuel cell. Since the fuel cell is normally operated at around 60 °C, we investigated the proton conductivity of the formed nanocomposite membranes as a function of the concentration in weight (wt%) of impregnated TiO_2 nanoparticles at 60 °C under different humidification conditions, as shown in Fig. 2. At fully hydrated state, the proton conductivity of

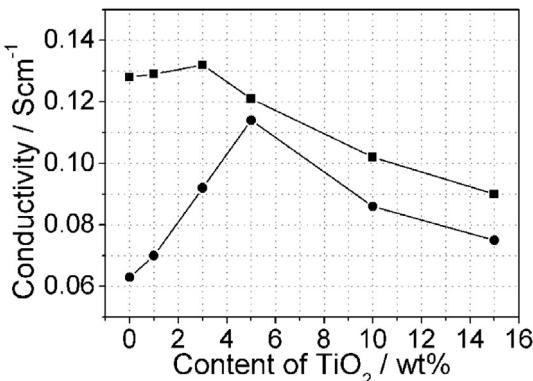


Fig. 2. Proton conductivity of composite membranes as a function of impregnated concentration of TiO_2 fillers under relative humidity of 100% (squares) and 50% (circles) at 60 °C. Solid lines are guide to eyes.

composite membranes initially increased slightly with the addition of hygroscopic TiO_2 nanoparticles up to 3 wt%. This slight increase in proton conductivity is possibly attributed to the increased surface hydroxyl groups on the well-distributed TiO_2 nanoparticles which are also proton carriers. With further increase the content of TiO_2 nanoparticles (above 5 wt%), the proton conductivity decreases since the less-proton-conductive fillers may block the proton transporting pathway inside the membrane [12]. However, the proton conductivity at relative humidity of 50% displayed a quite different behavior. At the concentration of impregnated TiO_2 fillers below 5 wt%, the proton conductivity values increase significantly with the increase in TiO_2 concentration, reaching 0.114 S cm^{-1} for the membrane with 5 wt% of TiO_2 fillers. With further increase in concentration of TiO_2 fillers, the proton conductivity decreases although the water uptake of composite membranes still increases, as shown in Fig. 3. It is hypothesized that the proton transporting channels can be opened at relative humidity of 50% with the impregnated concentration of TiO_2 fillers of about 5 wt% and the further added TiO_2 fillers may block the proton transporting pathway in the composite membranes. To elucidate the non-monotonic behavior of proton conductivity as a function of concentration of impregnated TiO_2 fillers at reduced humidification conditions, positron annihilation lifetime technique was applied.

Fig. 4 displayed the o-Ps lifetime and intensity of the formed composite membranes as a function of concentration of impregnated TiO_2 fillers at room temperature (30 °C) under relative humidity of 50%. The o-Ps annihilation lifetime τ_3 increases with the increase in the concentration of impregnated TiO_2 fillers, indicating the increase in size of free volume inside the formed membranes. However, the o-Ps annihilation intensity I_3 initially increases with the TiO_2 concentration. After reaching the maximum value of 4.9% with the sample having 5 wt% of TiO_2 fillers, the I_3 decreases with further increase in TiO_2 concentration. Since the impregnated hygroscopic metal oxide fillers located in the hydrophilic clusters through electrostatic interaction with sulfonic acid groups on Nafion [16,17], the initial increase in τ_3 below the TiO_2 concentration of 5 wt% can be attributed to the expansion of the ionic clusters in membranes by the impregnated TiO_2 fillers whereas the further increases in τ_3 at TiO_2 concentration above 5 wt% results from the increased particles size of TiO_2 and according interfacial areas of TiO_2 and sulfonic acid groups at relatively high concentration of TiO_2 fillers. The variation of particle size of TiO_2 at different concentrations of TiO_2 fillers was confirmed by TEM images shown as inset in Fig. 4. At TiO_2 concentration of 5 wt%, the formed particles with diameter of 3–7 nm were well distributed in the dispersion whereas large aggregates of TiO_2 with diameter above 10 nm were

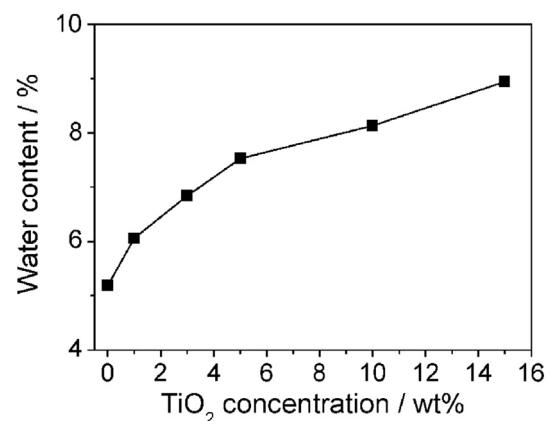


Fig. 3. Water uptake of composite membranes as a function of impregnated concentration of TiO_2 fillers under relative humidity of 100% at 60 °C.

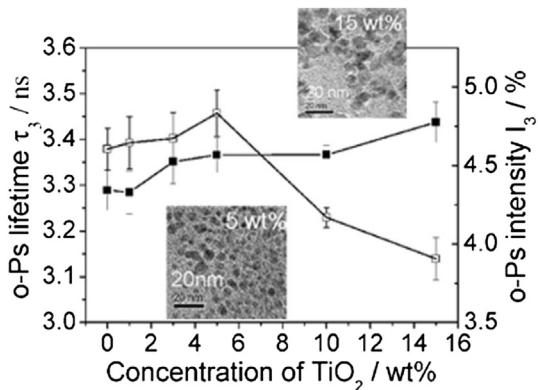


Fig. 4. o-Ps annihilation lifetime (solid squares) and intensity (open squares) of composite membranes as a function of TiO_2 fillers at 30°C under relative humidity of 50%. The insets are TEM images of TiO_2 nanoparticles at different TiO_2 fillers concentration as displayed on the figure.

observed for dispersion containing 15 wt% of TiO_2 . The particles with diameter around 5 nm could fill in the hydrophilic clusters and could help open the proton transporting channels. The increased number density of free volume can accordingly facilitate proton transportation in the membrane, leading to the enhanced proton conductivity [18]. In addition, the existing hydroxyl groups on TiO_2 nanoparticles located in hydrophilic channels in the membrane can also facilitate proton transport along the surface. For large particles impregnated in the membrane, although the size of free volume increased, the number density of free volume decreased dramatically as indicated by the o-Ps annihilation intensity, suggesting that the hydrophilic channels in the membranes were destroyed. Accordingly, the proton transporting efficiency decreased, leading to the decrease in the proton conductivity. Thus, proton conductivity of composite membranes exhibits a non-monotonic behavior with the concentration of impregnated TiO_2 fillers.

The interaction of in situ formed TiO_2 nanoparticles and Nafion molecules was further investigated using dynamic light scattering measurements. Fig. 5 displayed the hydrodynamic diameters of different Nafion– TiO_2 nanoparticles hybrids. For comparison, the hydrodynamic diameter of Nafion was plotted in the same figure. At TiO_2 nanoparticles concentration of 5 wt%, only one type of particle was observed at 220 nm that is much smaller than the size of aggregated Nafion chains (660 nm), indicating that Nafion molecules are covered at the surface of TiO_2 nanoparticles and the hybrids are evenly and well distributed in the dispersion. However,

two scattering peaks at about 56 nm and 312 nm were observed for hybrids containing 15 wt% of TiO_2 nanoparticles, indicating that Nafion molecules are not enough to cover the surface of in situ formed TiO_2 nanoparticles and aggregation of initial formed TiO_2 nanoparticles occurs. Similar phenomenon was observed for Nafion–silica hybrids in literature [19]. Subsequently, the aggregated large TiO_2 nanoparticles hinder the formation of ionic clusters during the membrane formation, leading to the decreased ion transporting efficiency for the formed membrane. This result is consistent with the PAL and TEM observation.

The effect of relative humidity on the proton conductivity and free volume was also investigated using the composite membrane with the impregnated TiO_2 concentration of 5 wt%. Fig. 6 displayed the proton conductivity and water uptake of the formed composite membrane as a function of environmental relative humidity. It is evident that the water uptake increases almost linearly with the relative humidity. However, the proton conductivity increased dramatically with the increases in relative humidity in the range from 0% to 50% whereas it only slightly increased from 0.114 S m^{-1} to 0.121 S cm^{-1} with the further increased humidity from 50% to 100%. This could be understood with the o-Ps annihilation lifetime τ_3 and intensity I_3 features, as shown in Fig. 7. It can be clearly seen that the τ_3 increases with the increase in relative humidity from 0% to about 50%, indicating the increase in size of free volume inside the membrane due to the expansion and the improved flexibility of polymer chains through absorbing water molecules [20,21]. In general, o-Ps annihilation intensity in perfluorinated polymer backbone is in the range of 10–20% [21]. The observed o-Ps annihilation intensity in this study is below 5%, suggesting that the formed o-Ps mainly annihilates by the sulfonate groups in the ion-rich region. Thus, the τ_3 and I_3 reflected the microstructures of the ionic cluster and the increased size of free volume in the composite membrane suggested the gradually formation of ionic clusters and opened proton transporting channels. Accordingly, the proton conductivity increased from 0.006 S cm^{-1} to 0.114 S cm^{-1} with the increase in relative humidity from 0% to 50%. With further increase in relative humidity, the excess water molecules started to fill in the free volume and the o-Ps annihilation in water may occur. Because the o-Ps annihilation lifetime in water ($\sim 1.8 \text{ ns}$) [22] is shorter than that in the formed free volume, the observed o-Ps annihilation lifetime decreased with the increase in relative humidity under the relative humidity above 50%. This result indicates that the Nafion– TiO_2 nanocomposite membrane with concentration of 5 wt% TiO_2 fillers can effectively transport protons under the relative humidity of 50% with which the hydrophilic ion clusters and the proton transporting channels are formed. This could be beneficial to fuel cell as fuel cells operated under low humidification conditions can

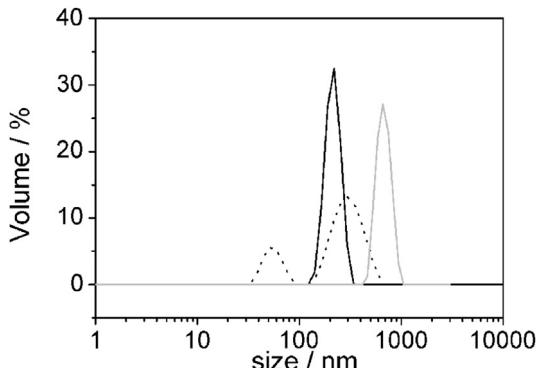


Fig. 5. Scattering distribution intensity of Nafion/ TiO_2 nanoparticles hybrids with different concentration of TiO_2 : 0 wt% (gray), 5 wt% (black solid), and 15 wt% (black dot).

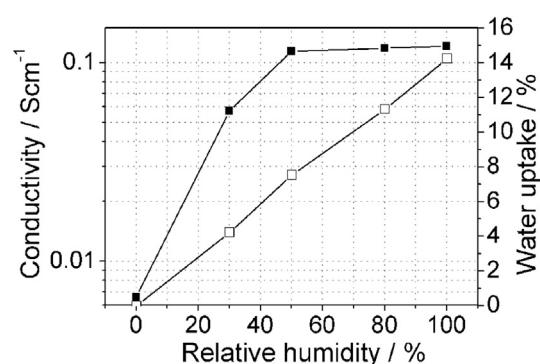


Fig. 6. Proton conductivity (solid squares) and water uptake (open squares) of composite membranes with TiO_2 fillers concentration of 5 wt% as a function of relative humidity at 30°C .

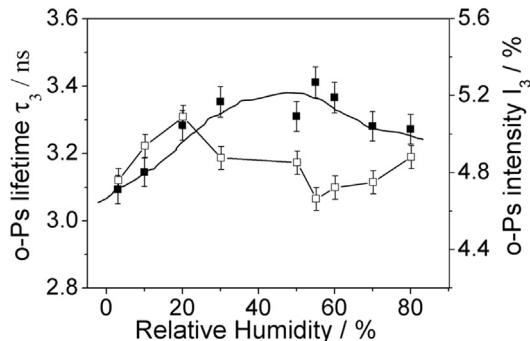


Fig. 7. o-Ps annihilation lifetime (solid squares) and intensity (open squares) of membrane with 5 wt% of TiO₂ fillers as a function of relative humidity at 30 °C.

not only increase the power density by simplify the system, but also enhance the durability of the membranes [23].

4. Conclusions

In summary, as a powerful tool for determination of microstructure of polymeric materials, positron annihilation lifetime study was applied for the investigation of polymer electrolyte membranes containing Nafion ionomers and TiO₂ nano-fillers. The correlation between electrochemical properties and the size and number density of the free volumes inside the membrane was established with the measurement of o-Ps annihilation lifetime and intensity. It was revealed that proton conductivity of the formed nanocomposite membranes exhibited non-monotonic behavior with the increase of the content of TiO₂ nano-fillers. The formed membrane with 5 wt% of TiO₂ nano-fillers showed the best electrochemical performance under reduced humidification conditions and it could be saturated by water molecules at the environmental relative humidity of about 50%, attributed to the micro-structural variation of composite membranes under different conditions.

Acknowledgments

This work was financially supported by The National Basic Research Program of China (Grant No. 2013CB932901, 2010CB923200), Program for New Century Excellent Talents in University, Fund of State Key Laboratory of Information Photonics and Optical Communications (Beijing University of Posts and Telecommunications, PR China), National Natural Science Foundation of China (Grant No. 61376018, 51372267, 51202286, 51172270, 51102019, 61177085, 51272031).

References

- [1] S. Srinivasan, Springer, Heidelberg, 2006.
- [2] K.A. Mauritz, R.B. Moore, Chem. Rev. 104 (2004) 4535.
- [3] T.J. Peckham, S. Holdcroft, Adv. Mater. 222 (2010) 4667.
- [4] S. Bose, T. Kuila, T.X.H. Nguyen, N.H. Kim, K.T. Lau, J.H. Lee, Prog. Polym. Sci. 36 (2011) 813.
- [5] H.W. Zhang, P.K. Shen, Chem. Rev. 112 (2012) 2780.
- [6] R.A. Mauritz, J.T. Payne, J. Membr. Sci. 168 (2000) 39.
- [7] N.H. Jalani, K. Dunn, R. Datta, Electrochim. Acta 51 (2005) 553.
- [8] Y. Devrim, S. Erkan, N. Bac, I. Eroglu, Int. J. Hydrogen Energy 37 (2012) 16748.
- [9] J.J. Pan, H.N. Zhang, W. Chen, M. Pan, Int. J. Hydrogen Energy 35 (2010) 2796.
- [10] G. Alberti, M. Casciola, Annu. Rev. Mater. Res. 33 (2003) 129.
- [11] H.F.M. Mohamed, K. Ito, Y. Kobayashi, N. Takimoto, Y. Takeoka, A. Ohira, Polymer 49 (2008) 3091.
- [12] W. Xie, H. Ju, G.M. Geise, B.D. Freeman, J.I. Mardel, A.J. Hill, J.E. McGrath, Macromolecules 44 (2011) 4428.
- [13] R.C. McDonald, D.W. Gidley, T. Sanderson, R.S. Vallery, J. Membr. Sci. 332 (2009) 89.
- [14] K. Sudarshan, S.K. Rath, M. Patri, A. Sachdeva, P.K. Pujari, Polymer 48 (2007) 6434.
- [15] G.B. Ye, K. Li, C.A. Xiao, W. Chen, H.N. Zhang, M. Pan, J. Appl. Polym. Sci. 120 (2011) 1186.
- [16] K. Li, G.B. Ye, J.J. Pan, H.N. Zhang, M. Pan, J. Membr. Sci. 347 (2010) 26.
- [17] H.L. Tang, M. Pan, J. Phys. Chem. C 112 (2008) 11556.
- [18] Y. Shibahara, H.S. Sodaye, Y. Akiyama, S. Nishijima, Y. Honda, G. Isoyama, S. Tagawa, J. Power Sources 195 (2000) 5934.
- [19] J.J. Pan, H.N. Zhang, M. Pan, J. Colloid Interface Sci. 326 (2008) 55.
- [20] D. Bamford, G. Dlubek, G. Dommet, S. Horing, T. Lupke, D. Kilburn, M.A. Alam, Polymer 47 (2006) 3486.
- [21] W. Huang, Y.S. Xu, X.J. Chen, X.L. Gao, Y.B. Fu, J. Radioanal. Nucl. Chem. 273 (2007) 91.
- [22] M. Eldrup, Ph.D. thesis, The Technical University of Denmark, Copenhagen, 1971.
- [23] H.L. Tang, P.K. Shen, S.P. Jiang, F. Wang, M. Pan, J. Power Sources 170 (2007) 85.